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Melting Mechanism in Monolayers of Flexible Rod-Shaped Molecules

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The melting of butane and hexane monolayers adsorbed on a graphite basal-plane surface has been studied by molecular-dynamics simulations and experimentally by neutron diffraction. The simulation results are qualitatively consistent with the observed diffraction patterns and suggest a general mechanism for melting in monolayers of flexible rod-shaped molecules. Melting requires the formation of vacancies in the monolayer by molecular motion perpendicular to the surface. This "footprint reduction" mechanism implies that strictly two-dimensional theories of melting are inapplicable to these systems.

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The subject of melting in two dimensions (2D) remains a controversial subject. Interest in the theory of 2D melting has been greatly stimulated by the work of Kosterlitz and Thouless, of Halperin and Nelson, and of Young (KTHNY) [1]. In this theory, melting may occur via two *continuous* transitions as opposed to a single first-order transition in three-dimensional (3D) systems. The first transition in the melting process involves the unbinding of dislocation pairs in the 2D solid and results in a fluid, termed the "hexatic phase," which has quasi-long-range bond-orientational order but short-range translational order. The second transition is from the hexatic phase to a normal, isotropic fluid with short-range orientational order.

Monolayers bound to solid surfaces by weak van der Waals forces and which are incommensurate with the substrate are generally believed to be systems to which the KTHNY theory should apply. Surprisingly, the simplest of such physisorbed systems, rare gases adsorbed on graphite basal-plane surfaces, have provided somewhat ambiguous experimental support for the theory [2]. Extensive computer simulations of rare-gas monolayers on graphite have been performed by Abraham [3]. His simulations are generally consistent with first-order melting and do not provide compelling evidence of the hexatic phase. However, these results must be interpreted cautiously since the hexatic phase is predicted to have long-range correlations and slow dynamics which are difficult to simulate properly.

It is perhaps equally surprising that, to date, only experiments with larger molecules, ethylene [4,5] and possibly ethane [6] on graphite, have exhibited heat capacity and dynamical signatures consistent with continuous melting. These hydrocarbon molecules possess steric properties and rotational degrees of freedom which one might expect to complicate the melting process.

For some time, we have been interested in how the melting of quasi-2D monolayers is affected by the steric properties of the constituent molecules [7]. The systems which we have been studying are rod-shaped molecules,

the *n*-alkanes $[\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_3]$, adsorbed on the basal-plane surfaces of graphite [7]. In particular, we have investigated the structure and melting of butane ($n=4$) and hexane ($n=6$) monolayers on graphite by neutron diffraction and by computer simulation. Since these rod-shaped molecules are identical in structure except for their length, they provide an excellent opportunity for studying steric effects on melting.

From our simulations of these systems, we propose here a general mechanism for melting of monolayers of flexible rod-shaped molecules which is consistent with the diffraction experiments [8]. Our evidence for this mechanism is based on a study of the molecular motions perpendicular to the surface and does not depend on the order of the melting transition which is extremely difficult to establish from simulations [3].

In Fig. 1 we show neutron diffraction patterns of butane [7,9] and hexane [7,10] monolayers adsorbed on an exfoliated graphite substrate. At low temperature, both monolayers have a rectangular unit cell containing two molecules arranged in a herringbone pattern [7,10,11].

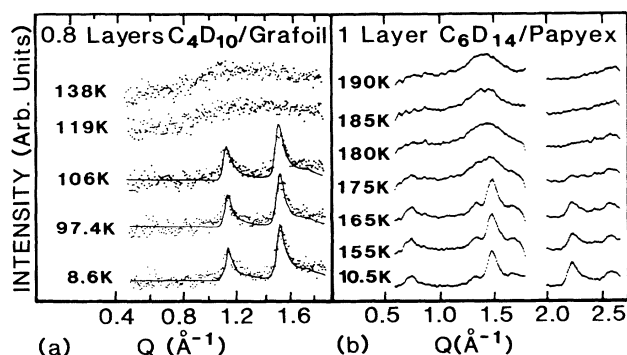


FIG. 1. Neutron diffraction patterns of two different alkane monolayers adsorbed on an exfoliated graphite substrate as the temperature is raised through the monolayer melting point: (a) 0.8 layer of deuterated butane (C_4D_{10}) (Refs. [7,9]); (b) 1.0 layer of deuterated hexane (C_6D_{14}) (Refs. [7,10]).

The molecules are in the trans conformation with the molecular plane parallel to the graphite basal-plane surface. This structure is illustrated for hexane in the simulation cluster of Fig. 2(a).

Upon heating, the butane monolayer displays an abrupt first-order melting. One sees in Fig. 1(a) that the intensity of the diffraction peaks remains unchanged up to a temperature of 106 K. By 119 K, the peaks have completely disappeared and have been replaced by a broad band of scattering attributed to the monolayer fluid. Diffraction scans taken at more closely spaced temperature intervals [9] show the peak intensities to decrease slowly above 108 K until they abruptly disappear at 116 K. Hysteresis was observed in the patterns within a few tenths of a degree about this temperature.

The diffraction patterns of the hexane monolayer in Fig. 1(b) show a qualitatively different behavior upon heating. There is little change in the diffraction patterns up to 155 K where the Bragg peaks of the herringbone structure begin to weaken. Above 175 K, peaks remain at $Q=0.8$, 1.4, and 2.5 \AA^{-1} which, while broader than those at low temperature, are considerably narrower than the single broad band observed from the fluid butane monolayer. Other measurements show that the peak at $Q=1.4 \text{ \AA}^{-1}$ is still observable at room temperature [10].

In order to elucidate the structure of the high-temperature phases of the butane and hexane monolayers, we began a series of molecular-dynamics simulations [8,12]. These have utilized the skeletal model of the alkane molecules developed in previous simulations of bulk alkanes [12-14] in which the methyl and methylene groups are replaced by single force centers or pseudoatoms at the carbon atom positions. The flexibility of the molecules is preserved by allowing the bend and dihedral-torsion angles of the molecule to vary; however, the fast stretching modes between pseudoatoms are neglected by fixing the bond lengths. The molecule-surface and intermolecular interactions are represented in the simulations by atom-atom potentials of the Lennard-

Jones 6-12 type. Within the molecule, a representation of the bend-angle and dihedral-torsion potentials due to Weber [13] was used. Since the bond lengths were fixed, a constraint dynamics scheme [15] was employed to integrate the equations of motion.

The simulations were performed on a monolayer cluster consisting of 128 and 104 molecules of butane and hexane, respectively. The simulation box size is $\sim 67 \times 67 \text{ \AA}^2$. This gives a maximum sample dimension of 90 \AA which lies in the middle of the range of observed monolayer coherence lengths (60 to 120 \AA) [9,10]. Initially, the monolayer clusters are in the zero-temperature configuration predicted by the potentials which, for both molecules, differs only slightly from the observed structure. Periodic boundary conditions are used in two orthogonal directions parallel to the surface.

The simulations were done at a fixed temperature (canonical sampling) with time steps of 0.002 ps (butane) and 0.001 ps (hexane) [16]. Thermodynamic functions and structural data are calculated as an average over time blocks of 10 ps with a sampling every 0.1-0.2 ps. The simulations last 150-350 ps. These long times are required for proper identification of the monolayer structure near a phase transition. The reader is referred to Refs. [8,15,17] for further details of the simulation method. Representative structures of the hexane monolayer cluster are illustrated in Fig. 2.

The results of the simulations are qualitatively consistent with the temperature dependence of the diffraction patterns of the two monolayers shown in Fig. 1. In the case of butane, the monolayer cluster is found to melt abruptly as observed but at $\sim 152 \text{ K}$, a temperature about 25% higher than found experimentally [18]. Consistent with the broad band of scattering in the diffraction pattern, the simulations indicate only short-range translational order above the melting point. In addition, they provide details of the orientational order and conformational state of the molecules in the fluid phase which cannot be extracted from the diffraction patterns: The plane containing the pseudoatoms of the molecules is, on the average, parallel to the surface; but the molecules are rotationally disordered about the surface normal. Furthermore, virtually all molecules remain in their trans conformation as the temperature is raised through the melting point.

In the case of hexane, the melting process is more complicated so that it is useful to begin by comparing the observed diffraction patterns with the temperature dependence of the spherically averaged structure factor $S(Q)$ computed in the simulation. Note that $S(Q)$ at a given temperature is calculated for a number of configurations and averaged over a time block as described above. We find that the change in $S(Q)$ near 225 K shown in Fig. 3 qualitatively reproduces the temperature dependence observed in the diffraction patterns of Fig. 1(b) [19]. The labeled Bragg peaks in the plot of $S(Q)$ at 210 K [Fig.

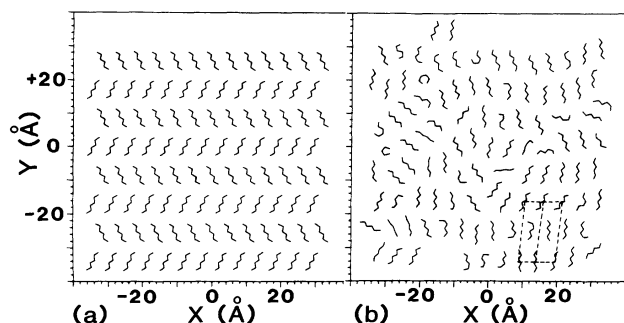


FIG. 2. Molecular configurations projected onto the graphite surface from the hexane monolayer simulations: (a) initial (zero-temperature) configuration obtained by minimizing the potential energy of the cluster; (b) structure at $T=225 \text{ K}$ just above the melting transition.

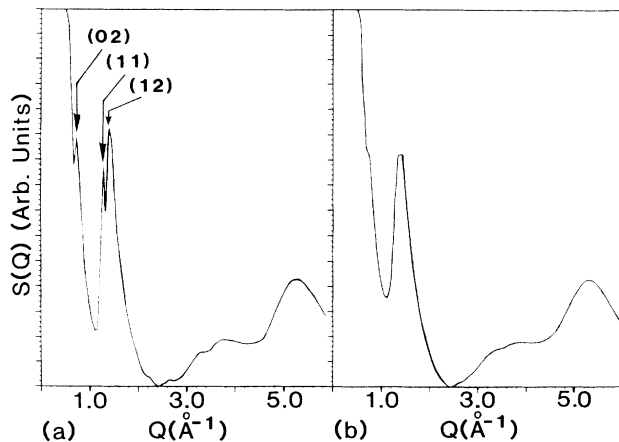


FIG. 3. Spherically averaged structure factor $S(Q)$ from the hexane monolayer simulations at two temperatures: (a) $T = 210$ K; (b) $T = 225$ K.

3(a)] are characteristic of the herringbone phase. They are replaced at 225 K [Fig. 3(b)] by a shoulder at $Q = 0.7 \text{ \AA}^{-1}$ and a wider peak at $Q = 1.4 \text{ \AA}^{-1}$ [20], features which can be identified with the broad peaks appearing above 175 K in the neutron diffraction patterns [21]. Associating this change in $S(Q)$ with monolayer melting yields a melting point at ~ 225 K. Analysis of the temperature dependence of the intermolecular potential energy and the in-plane molecular orientations is also consistent with melting of the hexane monolayer at this temperature so that, as for butane, the calculated melting point is $\sim 25\%$ higher than observed. Thus the simulations correctly predict the ratio of the butane-to-hexane monolayer melting points as determined by neutron diffraction [18].

Turning to the structure of the hexane monolayer above its melting point, we first note that the peak at $Q = 1.4 \text{ \AA}^{-1}$ in $S(Q)$ at 225 K [Fig. 3(b)] is about half the width of the peak which dominates $S(Q)$ at low Q in the simulation of the butane monolayer above its melting point [17]. This suggests that at high temperatures the hexane monolayer has a greater degree of translational order than does the butane monolayer. To obtain a specific model for the high-temperature structure of the hexane monolayer, it is helpful to examine more closely the molecular configurations in the simulation cluster at 225 K. As indicated by the dashed lines in Fig. 2(b), one finds patches of solidlike material having a rectangular-centered (RC) structure in which the molecules are in their trans conformation [22]. The patches are immersed in a fluid or disordered phase in which there is a significant concentration of gauche molecules. This interpretation is supported by the average Fourier transform of a sequence of structures generated within a time block. The transform so obtained at 225 K is plotted in Fig. 4(b) and shows both spots and rings consistent with coexisting solid and fluid phases. Note at 225 K the absence of both the (12) spot in the Fourier transform [Fig. 4(b)]

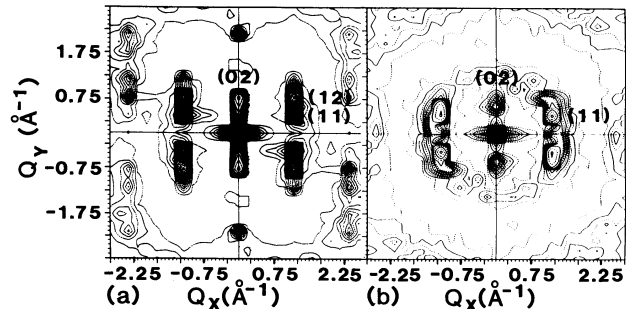


FIG. 4. Fourier transform of the hexane monolayer structure at the same temperatures as in Fig. 3: (a) $T = 210$ K; (b) $T = 225$ K.

and the (12) Bragg peak in $S(Q)$ [Fig. 3(b)] as required by the symmetry of the solid RC phase.

The two-phase model for the hexane monolayer at high temperatures suggested by the simulations can be tested by fits to the neutron diffraction patterns in Fig. 1(b) above 175 K. Profile analysis of these patterns [10] shows that the broad peaks observed can be indexed by an RC structure; however, the density inferred for the RC phase is (10–20)% greater than that of the low-temperature herringbone structure [23]. The simulations conducted thus far have not been on sufficiently large systems to be able to verify this density increase. Such calculations are now in progress [24].

We now consider the question of how the two monolayers, whose molecules differ only in length, can have qualitatively different melting behavior and high-temperature structures. The key, we believe, is in the formation of a significant number of gauche molecules in the hexane monolayer near melting as seen in the dihedral-angle distribution function (not shown) and the structure in Fig. 2(b). By colliding with their neighbors, the molecules acquire the energy necessary for this conformational change. This reduces the molecular footprint on the surface, creating vacancies within the monolayer solid which allow the molecules to rotate more freely and to disorder translationally. For the shorter butane molecule, we suggest that tilting is a more energetically favorable mechanism for vacancy formation than a conformational change. Collisions result in the lifting of one end of the molecule, allowing a neighboring molecule to rotate and translate underneath it. The tilt angles to create sufficient vacancies are rather small so that it is not necessary for the butane molecules to stand on end.

To substantiate this interpretation of the melting process for both monolayers, we have performed simulations in which the trans-gauche barrier is tripled in magnitude in order to prevent formation of gauche molecules. As expected, the melting point of the butane monolayer did not change since tilting was unaffected by the use of a rigid molecule. However, the melting point of the hexane monolayer increased by ~ 75 K [8]. Because no gauche molecules could be formed, vacancies were created by

tilting of the molecules which required greater thermal energy. The high-temperature structure of the hexane monolayer also changes on going from flexible to rigid molecules. Instead of solid-fluid coexistence, only a fluid phase with short-range translational and orientational order appears above the melting point. One sees patches in the simulation cluster consisting of a single row of trans molecules all pointing in the same direction [8].

We have also confirmed the role played by molecular tilting in the butane monolayer melting by performing simulations in which the magnitude of the molecule-substrate binding energy was tripled. This inhibited tilting and resulted in an increase of ~ 35 K in the monolayer melting temperature.

In summary, we emphasize that in both the butane and hexane monolayers considered here the long axis of these rod-shaped molecules remains orientationally ordered up to the melting transition. For such monolayers, our results suggest that the mechanism driving the melting process is vacancy creation caused by molecular motions perpendicular to the surface with the type of motion depending on the molecular aspect ratio. Thus we conclude that strictly two-dimensional theories of melting such as that of KTHNY are inapplicable to these systems. The same "footprint" reduction mechanism of vacancy formation may also occur in monolayers of other nonspherical molecules.

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- [16] These time steps were selected as a result of tests of energy conservation in microcanonical sampling near the melting points of both monolayers.
- [17] F. Y. Hansen, J. C. Newton, and H. Taub (unpublished).
- [18] The 25% discrepancy between the observed and simulated melting points for *both* the butane and hexane monolayers may reflect a deficiency of the skeletal model in representing both the intermolecular and molecule-substrate interactions.
- [19] The structure factor $S(Q)$ can only be compared qualitatively with the observed diffraction pattern since (a) it is calculated from the skeletal model of the molecules which does not contain the D atoms explicitly; (b) $S(Q)$ is spherically averaged so that it does not account for the preferential orientation of the graphite substrate particles; and (c) it does not contain instrumental resolution effects including the asymmetric Warren line shape imposed by the finite acceptance of the detector.
- [20] In the simulation, the peak which dominates $S(Q)$ at $Q=1.4 \text{ \AA}^{-1}$ is nearly twice as wide at 225 K as at 210 K in Fig. 3. This can be seen by noting that the "peak" at 210 K actually consists of the overlapping (11) and (12) peaks. At 225 K, only the (11) peak of the RC phase remains; its width is about twice that of each of the two overlapping peaks at lower temperature.
- [21] The peak in the neutron pattern near 2.5 \AA^{-1} in Fig. 1(b) does not appear in the calculated $S(Q)$ of Fig. 3(b) due to the neglect of the D atoms in the skeletal model [see (a) in Ref. [19]] the effect of which increases at higher Q . The large peak calculated in $S(Q)$ at $Q=0$ results from the finite size of the simulation box. It should be observable in the neutron pattern, since the monolayer particles are of comparable size to the simulation box. However, in practice, it is obscured in the process of subtracting the large small-angle scattering from the graphite substrate.
- [22] Consistent with the RC structure, the distribution of in-plane molecular-axis orientations has a single peak somewhat broader than the two peaks found for the low-temperature herringbone structure (see Refs. [8,17]).
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